



The effect of different divalent cations on the reduction of hexavalent chromium by zerovalent iron

Meifang Hou^{*}, Hongfu Wan, Tinglin Liu, Yanning Fan, Xinming Liu, Xugang Wang

Guangdong Key Laboratory of Agricultural Environment Pollution Integrated Control,
Guangdong Institute of Eco-environment and Soil Science, 510650 Guangzhou, China

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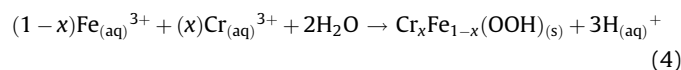
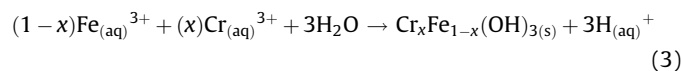
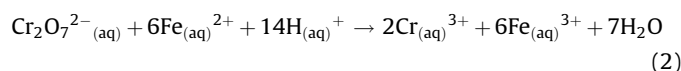
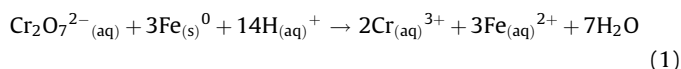
ABSTRACT

The effects of ferrous cation (Fe^{2+}), copper cation (Cu^{2+}) and calcium cation (Ca^{2+}) on the reduction of hexavalent chromium Cr(VI) by zerovalent iron (Fe^0) were investigated. The pseudo-first-order kinetic model was used for describing the reduction of Cr(VI) . The experimental results showed that Cu^{2+} and Fe^{2+} could improve the reduction of Cr(VI) but Ca^{2+} might inhibit the reduction of Cr(VI) by Fe^0 . The improvement of the reduction of Cr(VI) by Cu^{2+} on Fe^0 might be ascribed to Cu^{2+} acting as a catalyst or the media of charge transfer during the reaction. Different concentration of Cu^{2+} might lead to the different reduction kinetics of Cr(VI) by Fe^0 . The X-ray diffraction (XRD) results showed that the reacted iron powder was coated by a small amount of $\beta\text{-FeOOH}$. The results of scanning electron microscope (SEM), energy dispersive X-ray spectrometer (EDS) and Fourier-transform infra-red (FTIR) showed that the Fe-Cr coprecipitate or Fe-Cr-Cu coprecipitate might be formed during the reaction.

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1. Introduction

Chromium is a significant toxic inorganic contaminant, which was mainly derived from fossil fuel combustion, textile dyeing, metallurgy, wood preserving and petrochemical refining [1–3]. Although oxidation states of chromium range from -4 to $+6$, the $+3$ and $+6$ states, designated Cr(III) and Cr(VI) , are the two stable oxidation states in the environment. Cr(VI) attracted much attention because of its carcinogenicity, toxicity and high mobility [4,5]. Different from Cr(VI) , Cr(III) is less toxic and less mobile. Thus, the decontamination of waters or soil with Cr(VI) is much focused on and is usually realized by the reduction of Cr(VI) followed by chemical precipitation, adsorption, electrokinetic remediation and bioremediation [6–9]. In recent years, the use of zerovalent iron (Fe^0) for reduction of redox active metals is a promising alternative method [7,10–15]. The reduction of Cr(VI) by Fe^0 generally produces Cr(III) (Eqs. (1) and (2)), which may be further removed through the precipitation of Cr(OH)_3 or coprecipitation of mixed Fe(III)-Cr(III) hydroxide solid solution or mixed Fe(III)-Cr(III) oxyhydroxide solid solution (Eqs. (3) and (4)):



There are various parameters influencing the reduction kinetic of Cr(VI) by Fe^0 , which include the iron surface area, the pH value of the bulk phase, the ionic strength of the solution, and so on. In the environment, different cations may coexist with Cr(VI) and they may play the important roles in the removal of Cr(VI) [16,17]. Eary et al. [18] reported that chromate could be removed from aqueous wastes by reduction with ferrous ion (Fe^{2+}) (Eq. (2)) under the effect of different anions, and the products of the reduction of Cr(VI) by Fe^{2+} will be precipitated as hydroxide solids in slightly acidic to alkaline solutions depending on their solution concentrations (Eq. (3)), which suggested that Fe^{2+} is an effective reductant for the removal of Cr(VI) . It is also reported that there is an optimal pH value for Cr(VI) co-removal with mixed Cu^{2+} , Zn^{2+} and Ni^{2+} precipitation [17]. However, there is few report about the reduction behavior of Cr(VI) by Fe^0 in the presence of different cations, although the various cations may coexist with Cr(VI) for in situ reduction by Fe^0 , especially for the redox active cations (Fe^{2+} , Cu^{2+} , etc.) in the system. Thus, the study of

^{*} Corresponding author. Tel.: +86 20 87024871; fax: +86 20 87024123.
E-mail address: mfhoul@soil.gd.cn (M. Hou).

the effect of Fe^{2+} as an usual active reductant and Cu^{2+} as an usual active oxidant on the reduction of Cr(VI) by Fe^0 will provide a new sight for the practical removal of Cr(VI) by zerovalent iron.

Calcium (Ca^{2+}) is an important major cation present in the environment, which competes with trace metal ions for the binding sites of the active surface of metal oxide or hydroxide colloids in soil and water [19]. Iron in contact with air and aqueous solution is always covered by a layer of surface oxides or hydroxides, which have important influences on the reductive removal of pollutants by Fe^0 [20,21]. The interaction of Ca^{2+} , Cu^{2+} , Fe^{2+} , and etc with iron oxides or hydroxides may largely control the availability and mobility of metal ions and influence the properties of iron oxides or hydroxides [22–26], which might lead to different effects of metal ions on the removal process of Cr(VI) by Fe^0 .

The objective of this study is to investigate the effect of different cations on the reduction of Cr(VI) by Fe^0 . To avoid the complexing effect of the buffering chemicals on the behavior of metal cation, HCl and NaOH were selected for modifying the initial pH value of the reaction solution. When NaCl was used as the background electrolyte, Fe^{2+} as an active reductant, Cu^{2+} as an active oxidant and Ca^{2+} as the inert cation were selected in the experiments, among which the effect of Cu^{2+} concentration on the reduction of Cr(VI) by Fe^0 was concentrated since the combined pollution of Cr and Cu mostly exist in soil and waters and there are strong interaction of multipollutants upon their geochemical behaviors [27]. The work will be meaningful for in situ remediation of Cr(VI) pollution by Fe^0 in the environment.

2. Materials and methods

2.1. Materials

The zerovalent iron (Fe^0) powder of 100 mesh was purchased from Tianjin Kermel Chemical Reagent Development Center, China. The specific surface area of the Fe^0 powder measured by BET analysis and N_2 adsorption was $7.5 \text{ m}^2/\text{g}$. All chemicals including NaCl , $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, CaCl_2 , HCl and NaOH were obtained in analytical grade from Shanghai Chemical Co., China and were used as received without further purification.

The sources of Cr(VI) (Cr^{6+}), Fe^{2+} , Cu^{2+} and Ca^{2+} in the experiments were the freshly prepared stock solutions by dissolving the desired amounts of $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and CaCl_2 in deionized water. The water used for dissolving the salts was firstly purged with N_2 of high purity for removal of O_2 and CO_2 . If specification, the experiments were done in the darkness with 0.1 M NaCl as the background electrolyte.

2.2. Batch experiments of Cr(VI) by Fe^0

The batch experiments were carried out in a 250 ml flask under N_2 at room temperature (298 K). The reaction of Cr(VI) with Fe^0 was investigated under different divalent cations. The initial pH of the solution of Cr(VI) was adjusted by 1.0 M HCl and 1.0 M NaOH . In the experiments, the solution of Cr(VI) with the desired initial pH was firstly purged with N_2 for 30 min, and then put the Fe^0 powder and the solution of the target additional cations into the reaction solution under the vigorous stirring. The suspensions samples were taken at different time intervals and then separated by centrifugation at 4500 rpm for 30 min to get the supernatant and the sediment for analysis.

2.2.1. Effect of different divalent cation on the reduction of Cr(VI) by Fe^0

The effect of different divalent cation on the reduction of Cr(VI) was investigated with 0.40 g Fe^0 in the 200 ml solution under pH 3.00. The concentrations of Fe^{2+} , Cu^{2+} and Ca^{2+} in the initial

reaction concentration was up to 0.20 mM which is a little higher than the mole concentration of Cr(VI) with the initial concentration of 0.19 mM .

2.2.2. Effect of Cu^{2+} dose on the reduction of Cr(VI) by Fe^0

The effect of Cu^{2+} dose on the reduction of Cr(VI) was also examined with 0.40 g Fe^0 in the 200 ml solution under pH 3.00. 0.02 mM , 0.05 mM , 0.10 mM , 0.20 mM and 1.00 mM as different initial concentration of Cu^{2+} were involved in the experiments.

2.3. Chemical analyses

The concentration of Cr(VI) in the solution was quantified by the diphenylcarbazide colorimetric method with UV–vis spectrophotometry (TU1800-PC, Beijing). The concentration of Fe^{2+} and total iron in the solution was determined colorimetrically according to the phenanthroline method with UV–vis spectrophotometry (TU1800-PC, Beijing). The pH of the reaction solution during the experiments was detected by the pH meter (PHS-3, Shanghai).

The surface morphologies and surface elemental information of the Fe^0 powder before and after reaction were investigated by the Scanning electron micrograph and energy dispersive X-ray spectrometer (JSM-5910 Microscope and Noran EDS, Japan). The X-ray powder diffraction (XRD) was used for characterization with a Rigaku D/max 2500 diffractometer using $\text{Cu K}\alpha$ radiation; the accelerating voltage was 30 kV and the emission current was 30 mA . The Fourier-transform infra-red (FTIR) spectra were recorded as KBr pellets in the spectral range $4000\text{--}400 \text{ cm}^{-1}$ on a PerkinElmer 1725X FTIR spectrometer in air at room temperature.

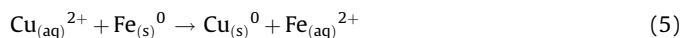
3. Results and discussion

3.1. Effect of divalent cations

The effects of Fe^{2+} , Cu^{2+} and Ca^{2+} on the reduction of Cr(VI) by Fe^0 were investigated and the experimental results were shown in Fig. 1. It can be seen that Fe^{2+} and Cu^{2+} obviously improved the reduction of Cr(VI) by Fe^0 but Ca^{2+} might have a little passive effect on the reduction of Cr(VI) by Fe^0 , which might be ascribed to different redox properties of the selected divalent cations involved in the reduction process of Cr(VI) by Fe^0 . According to the pseudo-first-order kinetic model, the reduction kinetic parameters of Cr(VI) by Fe^0 under the effects of Fe^{2+} , Cu^{2+} and Ca^{2+} of 0.20 mM and without the extra-addition of cation were $73.89 \times 10^{-3} \text{ min}^{-1}$ ($R = 0.965$), $57.43 \times 10^{-3} \text{ min}^{-1}$ ($R = 0.965$), $37.54 \times 10^{-3} \text{ min}^{-1}$ ($R = 0.988$) and $47.52 \times 10^{-3} \text{ min}^{-1}$ ($R = 0.976$), respectively.

Fig. 2 showed the changes of the ferrous ion concentration in the reaction solution and the total iron ion concentration in the reaction solution, respectively. The pH of the reaction solution during the reduction of Cr(VI) by Fe^0 increased from 3.00 to 4.71 ± 0.02 , 4.40 ± 0.03 , 4.92 ± 0.03 and 4.80 ± 0.07 for 1 h under the effects of Fe^{2+} , Cu^{2+} and Ca^{2+} of 0.20 mM and without the extra-addition of cation, respectively.

It can be seen that the corrosion rate of iron was greatly enhanced by the addition of Cu^{2+} , which might lead to more Fe^{2+} available in the reaction solution (Eq. (5), Fig. 2). Moreover, Fe^{2+} can be further oxidized into Fe^{3+} (Eq. (2)), which might result in the higher amount of total iron ion in the reaction solution (Fig. 2). As shown in Eq. (2), the reduction of Cr(VI) can be conducted effectively in the presence of Fe^{2+} [18]:



Usually, there is the corrosion of zerovalent iron (Fe^0) in the acidic solution, though Cr(VI) is absent. In the presence of Cu(II) , the

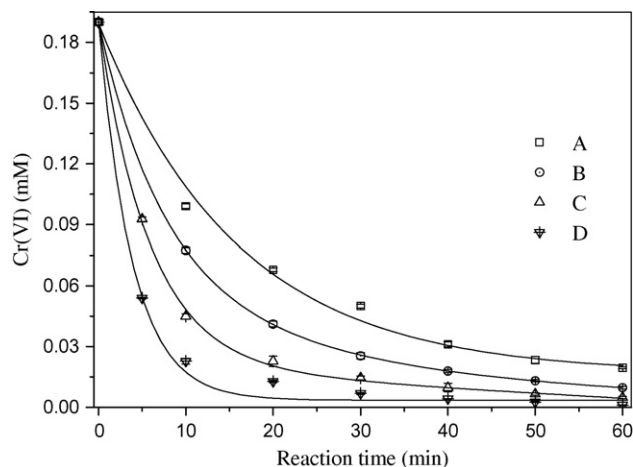


Fig. 1. The reduction of 0.19 mM Cr(VI) by Fe⁰ of 2.0 g/l at initial pH 3.00 under the effect of 0.20 mM Ca²⁺ (A), without the addition of cations (B), and the effects of 0.20 mM Cu²⁺ (C) and 0.20 mM Fe²⁺ (D).

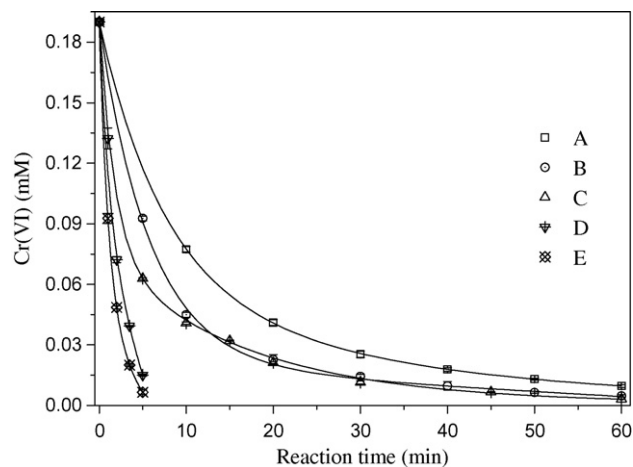


Fig. 3. The reduction of 0.19 mM Cr(VI) by Fe⁰ of 2.0 g/l at initial pH 3.00 under the Cu²⁺ effects of 0.00 mM (A), 0.20 mM (B), 0.02 mM (C), 0.05 mM (D) and 0.10 mM (E).

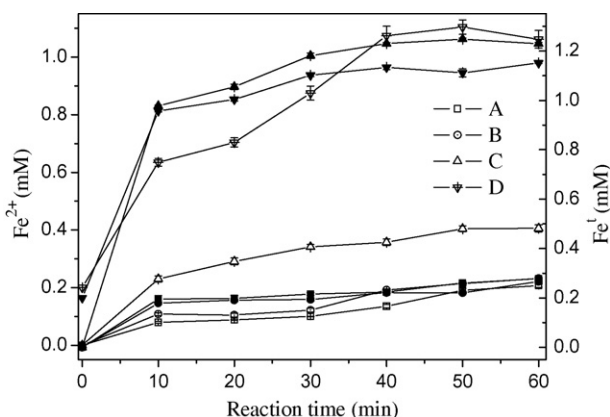


Fig. 2. The Fe²⁺ concentration (hollow legends) and the total iron ion concentration (solid legend) in the reaction solution of the reduction of 0.19 mM Cr(VI) by Fe⁰ of 2.0 g/l at initial pH 3.00 under the effects of Fe²⁺ (A), Cu²⁺ (B), without the addition of cations (C) and Ca²⁺ (D) of 0.20 mM.

corrosion of Fe⁰ was strengthened. As shown in Fig. 2, a large amount of hydrogen and Fe(II) can be produced during the corrosion of Fe⁰. The large amount of Fe(II) produced (~1.2 mM) in the presence of added Fe(II) and Cu(II) might be ascribed to the serious corrosion of Fe⁰, which might lead to the disproportion of the stoichiometric ratio between consumed Cr(VI) and produced Fe(II).

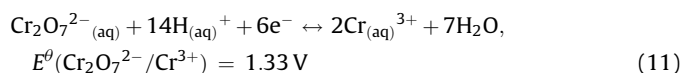
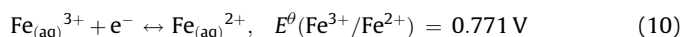
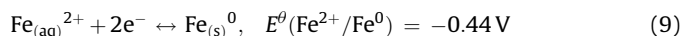
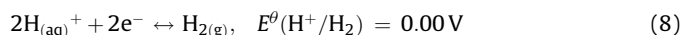
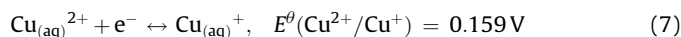
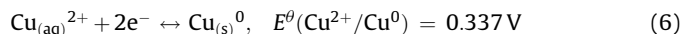
It is reported that there might be several reductants for removal of reducible pollutants by Fe⁰ in the reaction system, such as Fe⁰ itself, hydrogen, Fe²⁺, and Fe²⁺ might play more role than Fe⁰ and hydrogen in the reduction process of Cr(VI). When Cu²⁺ was added into the reaction solution, the corrosion of Fe⁰ enhanced the concentration of Fe²⁺ increased greatly. Thus, it can be deduced that there might be an obvious effect of Cu²⁺ on the reduction of Cr(VI). Since there is usually coexistence of Cr(VI) with Cu²⁺ in the contaminated environments, it is meaningful to investigate the effect of Cu²⁺ on the reduction of Cr(VI) by Fe⁰. Thus, the effect of Cu²⁺ on the reduction of Cr(VI) under different conditions were focused on in the following experiments.

3.2. Different concentration of Cu²⁺

0.02 mM, 0.05 mM, 0.10 mM and 0.20 mM as different initial concentration of Cu²⁺ were involved in the experiments. As shown in Fig. 3, the extra-addition of Cu²⁺ was favorable for the

improvement of the reduction of Cr(VI) by Fe⁰, and there was an optimal concentration of Cu²⁺ (0.10 mM) for the reduction of Cr(VI) by Fe⁰. According to the pseudo-first-order kinetic model, the reduction kinetic parameters of Cr(VI) by Fe⁰ under the effects of Cu²⁺ of 0.02 mM, 0.05 mM, 0.10 mM and 0.20 mM and without the extra-addition of Cu²⁺ were $60.75 \times 10^{-3} \text{ min}^{-1}$ ($R = 0.965$), $504.95 \times 10^{-3} \text{ min}^{-1}$ ($R = 0.998$), $659.66 \times 10^{-3} \text{ min}^{-1}$ ($R = 0.999$), $57.43 \times 10^{-3} \text{ min}^{-1}$ ($R = 0.965$) and $47.52 \times 10^{-3} \text{ min}^{-1}$ ($R = 0.976$), respectively. The concentration of Fe²⁺ and total iron ion in the reaction solution with respect to the reaction time were shown in Fig. 4. It can be deduced that the products of Fe²⁺ and Fe³⁺ were influenced by the addition of Cu²⁺. The change of pH value of the reaction solution with the addition of Cu²⁺ was lower than that without the addition of Cu²⁺.

In the acidic solution, the redox reaction of different cations were shown in the following equations (Eqs. (6)–(11)), Cr₂O₇²⁻ has the highest oxidative ability and Fe⁰ has the highest reductive ability. The reduction of Cr(VI) could happen directly by Fe⁰ leading to Cr(III), when the fresh surface of Fe⁰ derived from the removal of the iron oxides or hydroxides by H⁺ in the acidic solution:



Generally, the reductive transformation of pollutants is thermodynamically favorable under anaerobic conditions, but these reactions are often kinetically limited. Transition metal complexes have been shown to be the effective catalysts for redox reactions, especially when the catalytic effect has been attributed to facilitated transfer of electrons from a bulk reductant to the oxidant of interest through a cycling of the metal between reduced and oxidized forms [28]. Cu²⁺ has been shown to catalyze the reduction of nitrate by Fe²⁺ [29] and the dechlorination of

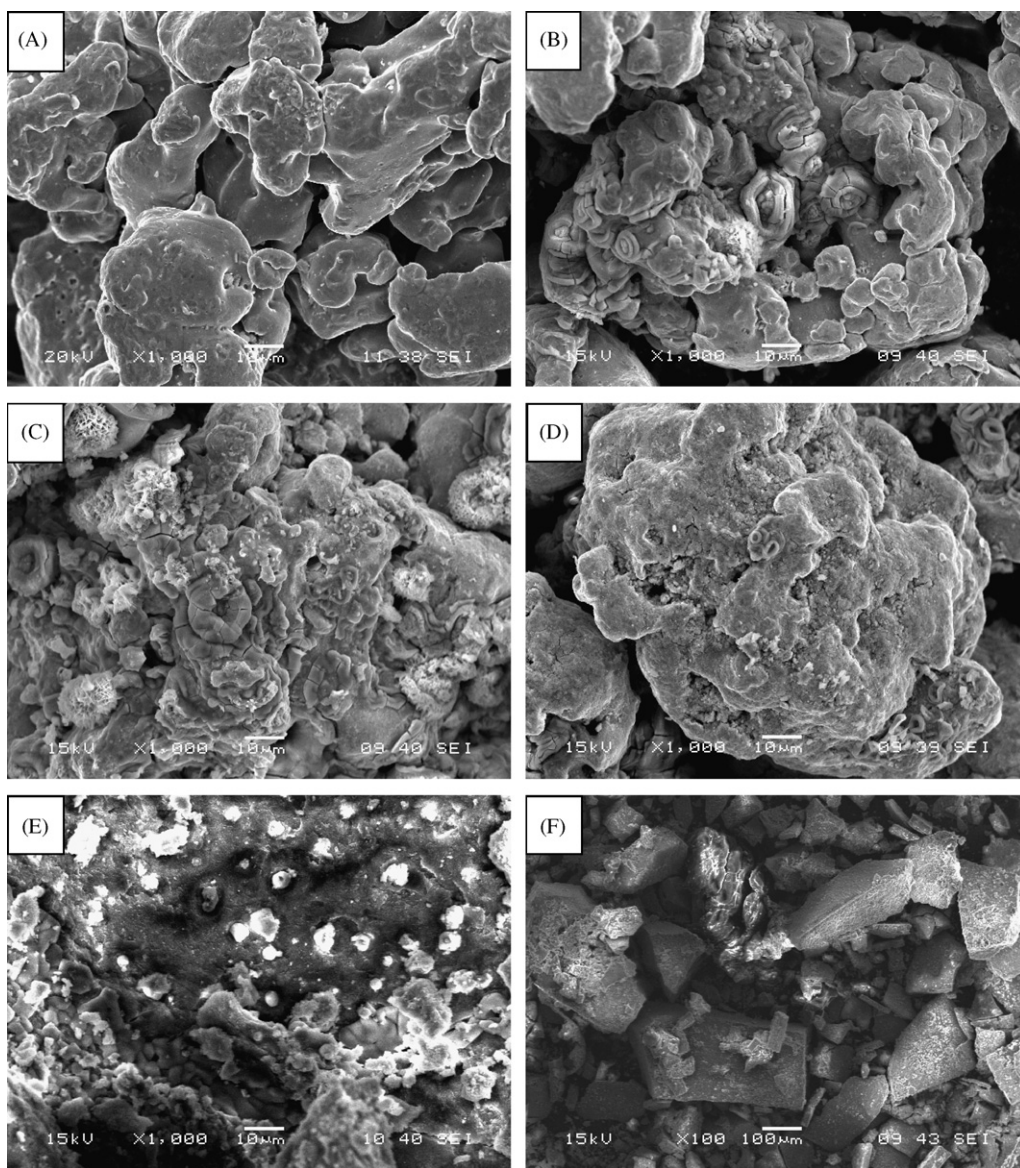


Fig. 6. SEM patterns of the raw iron powder (A), the collected iron powder after its reaction with 0.19 mM Cr(VI) (B), Cr(VI) (0.19 mM) + Cu (0.02 mM) (C), Cr(VI) (0.19 mM) + Cu (0.10 mM) (D) and the suspension powder in the reaction of iron with Cr(VI) (0.19 mM) + Cu (0.20 mM) (E and F).

The XRD patterns of the raw iron powder, the collected iron powder after its reaction with 0.19 mM Cr(VI), Cr(VI) and Cu (0.10 mM), Cr(VI) and Cu (0.20 mM) and the suspension powder in the reaction of iron with Cr(VI) and Cu (0.20 mM) were shown in Fig. 8. Three major peaks at 2θ values of 44.67° , 65.02° and 82.33° were assigned to Fe^0 [40], the weak peak at 2θ value of 14.2° to γ -FeOOH, the weak peak at 2θ value of 21.2° to α -FeOOH, the weak peak at 2θ value of 35.4° to magnetite, and the weak peak at 2θ value of 26.7° to β -FeOOH [21,33,40]. There was not the obvious diffraction peaks attributed to Cu_2O and CuCl , which might be due to the low amount and the low crystallinity compared with Fe^0 , iron oxides or hydroxides.

There might be little CuCl deposited on the iron surface since the XRD data did not show the obvious existence of CuCl in the experiments. Highly soluble and stable complexes $[\text{CuCl}_x]^{(x-1)-}$ may be formed when Cu(II) is reduced to Cu(I) in the presence of the Cl^- excess [41], since the complexes of Cu(I) and Cl(I) (e.g. $\log \beta_2([\text{CuCl}_2]^-) = 5.5$) is more stable than the complexes of Cu(II) and Cl(I) (e.g. $\log \beta_4([\text{CuCl}_4]^{2-}) = -4.6$). Thus, there might be the

stable complexes $[\text{CuCl}_x]^{(x-1)-}$ formed in the reaction solution in the presence of the Cl^- excess but little crystal CuCl deposited on the iron surface.

The α -FeOOH called goethite, β -FeOOH called akaganeite and γ -FeOOH called lepidocrocite in mineral names usually form from corrosion of iron in the aqueous solutions [42]. Compared with other iron oxides or hydroxides, β -FeOOH might be more easily developed when NaCl was selected as the background electrolyte and HCl was used for modifying the initial pH value of the reaction solution in the experiments [43]. It is reported that magnetite is the effective reductant for Cr(VI) [44] and lepidocrocite can act as a substrate for precipitation of Cr(OH)_3 and/or $\text{Cr}_x\text{Fe}_{1-x}(\text{OH})_3$ [45]. As seen in Fig. 8, when Cu^{2+} was in the reaction solution, magnetite might be easily formed on the surface of iron powder, and lepidocrocite would be formed on the surface of iron powder when Cu^{2+} of the higher concentration was involved in the reaction, which might favor the reduction of Cr(VI) by Fe^0 . Thus, iron oxides or hydroxides (α -FeOOH, β -FeOOH, γ -FeOOH, etc.) might form on the surface of the reacted Fe^0 powder during the reaction. In the

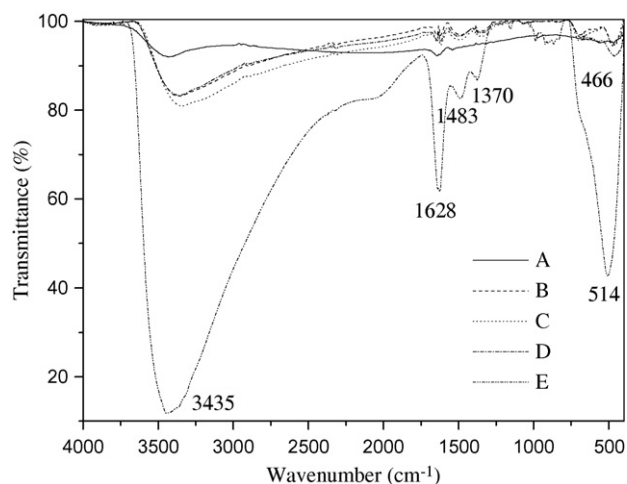


Fig. 7. FTIR spectra of the raw iron powder (A), the collected iron powder after its reaction with 0.19 mM Cr(VI) (B), Cr(VI) (0.19 mM) + Cu (0.02 mM) (C), Cr(VI) (0.19 mM) + Cu (0.10 mM) (D) and the suspension powder in the reaction of iron with Cr(VI) (0.19 mM) + Cu (0.20 mM) (E).

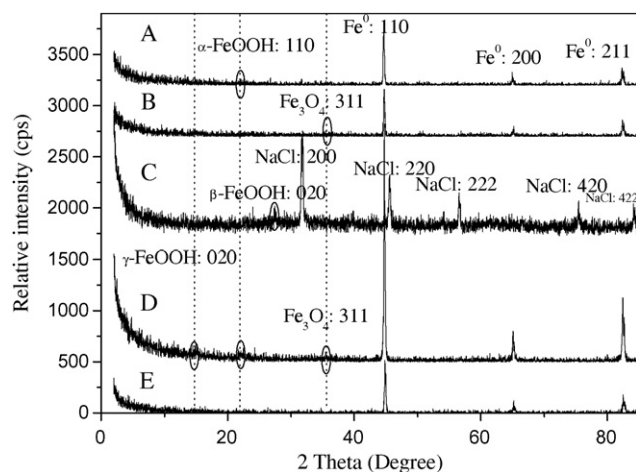


Fig. 8. XRD patterns of the collected iron powder after its reaction with 0.19 mM Cr(VI) (A) and Cr(VI) (0.19 mM) + Cu (0.02 mM) (B), the suspension powder in the reaction of iron with Cr(VI) (0.19 mM) + Cu (0.20 mM) (C), the collected iron powder after its reaction with Cr(VI) (0.19 mM) + Cu (0.10 mM) (D) and the raw iron powder (E).

presence of Cu^{2+} , magnetite and/or lepidocrocite might be formed on the surface of iron powder, which can improve the reduction of Cr(VI) by Fe^0 .

4. Conclusions

Fe^{2+} and Cu^{2+} had the positive effects but Ca^{2+} might have a little negative effect on the reduction of hexavalent chromium by zerovalent iron. Cu^{2+} might act as a catalyst or the media of charge transfer improving the reduction of Cr(VI) by Fe^0 . During the reaction, the Fe–Cr coprecipitate or Fe–Cr–Cu coprecipitate might be formed. The work might provide a new sight for the in situ removal of Cr(VI) by Fe^0 when Cu^{2+} coexists with Cr(VI) in the environments.

Acknowledgements

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